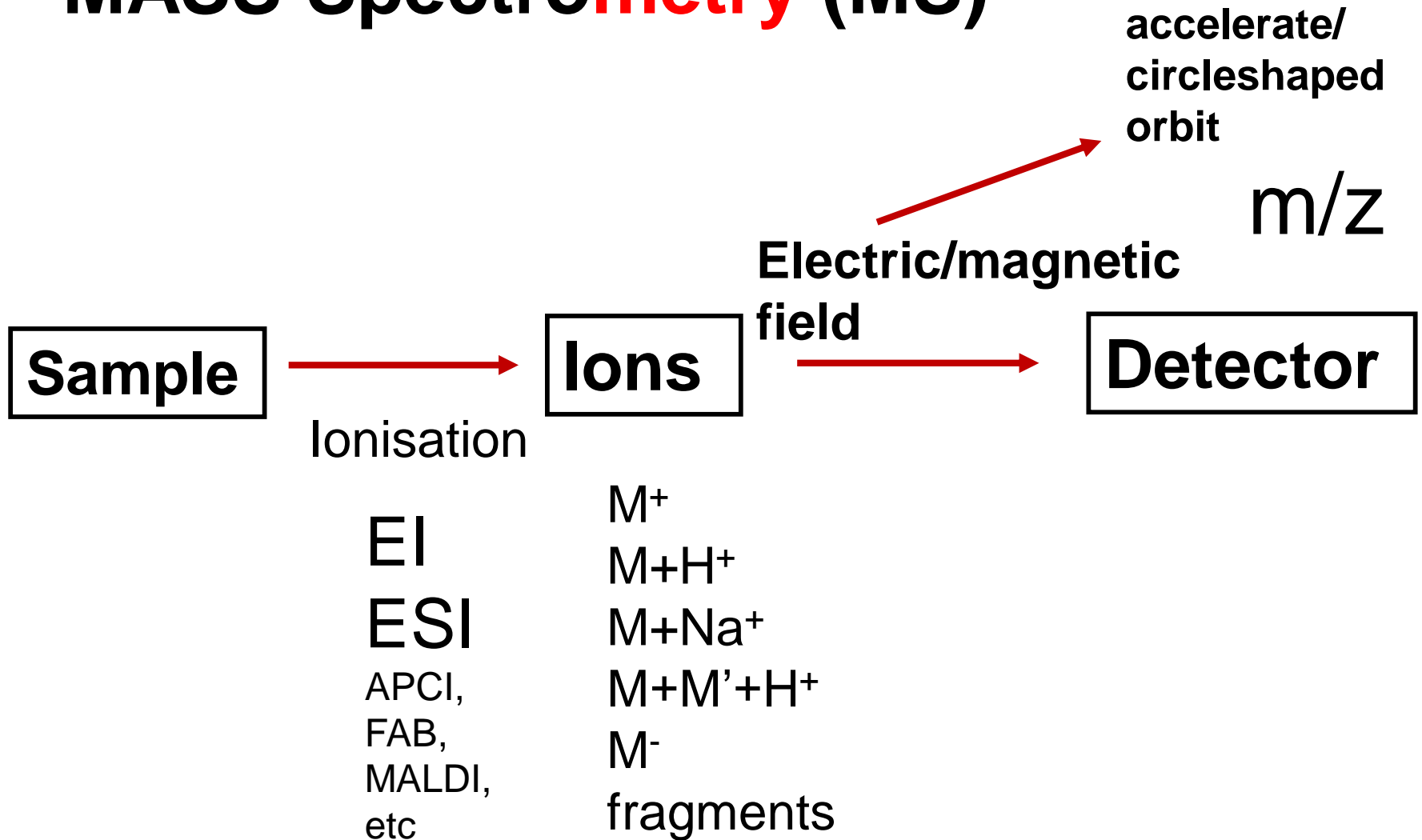
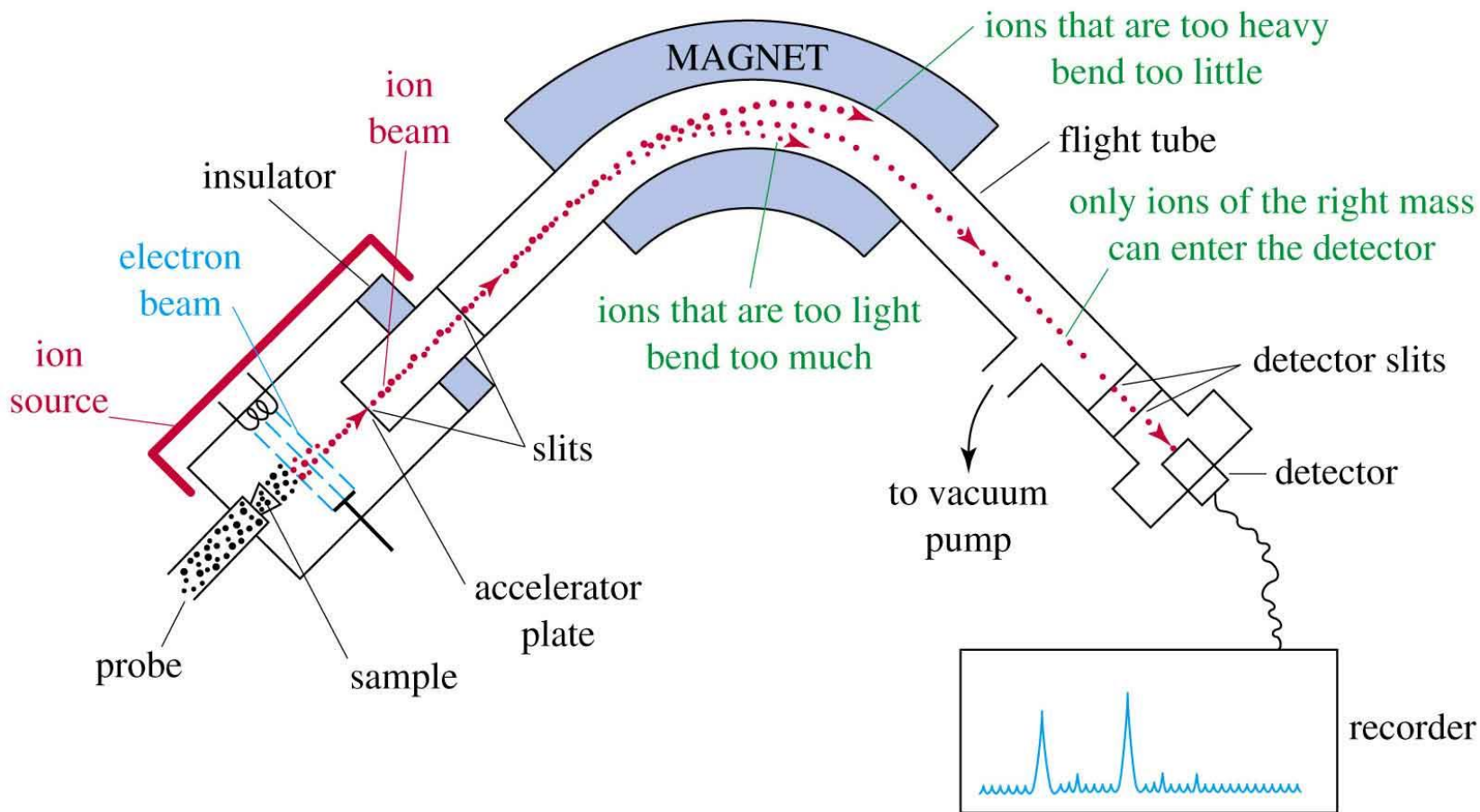
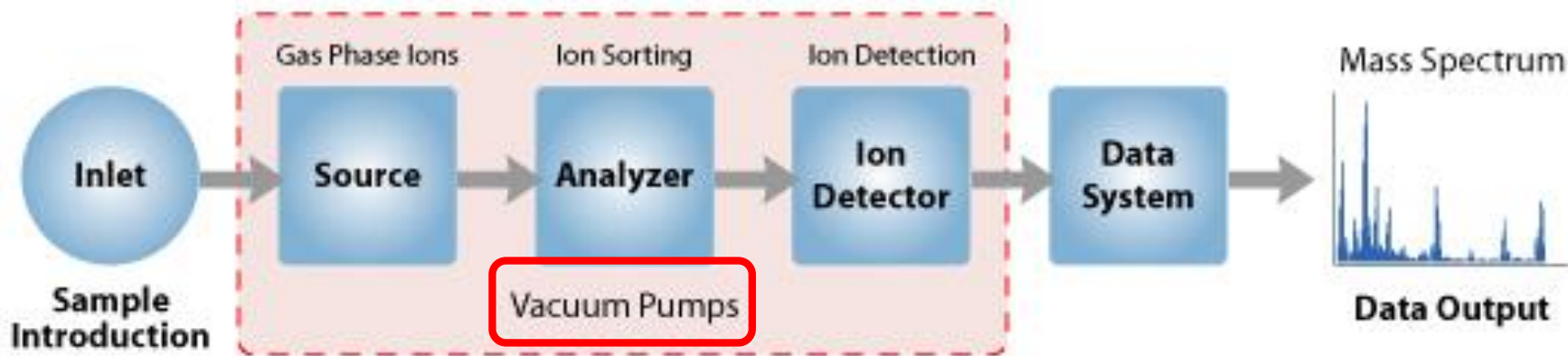


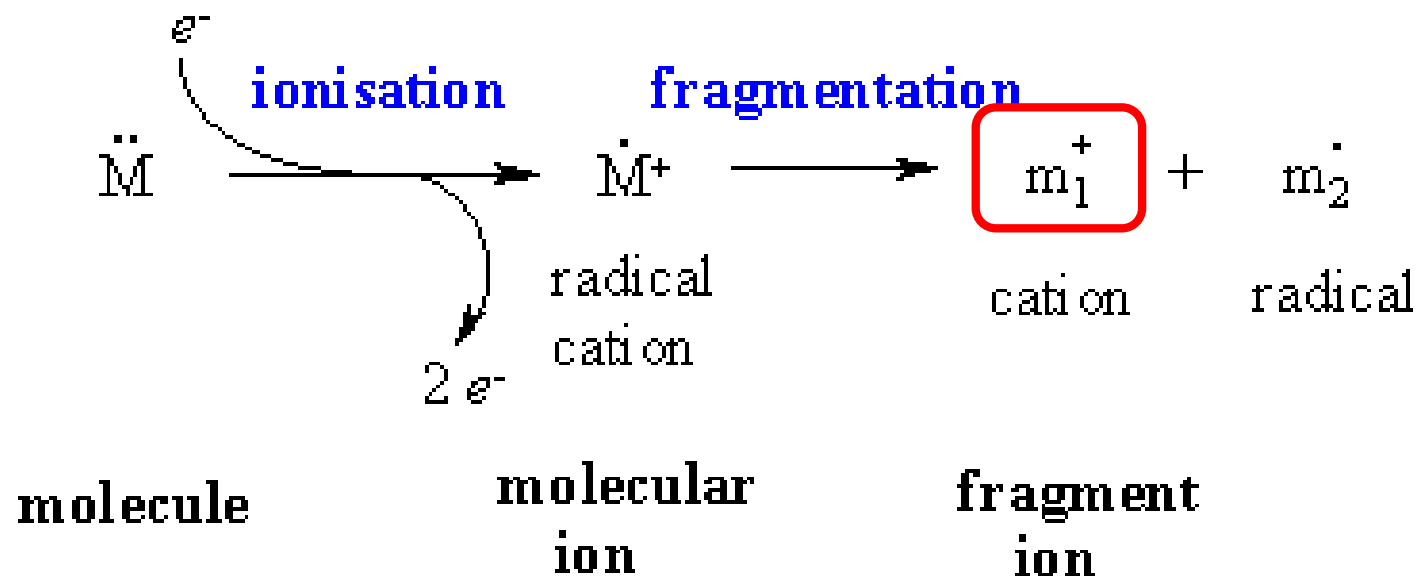
MASS Spectrometry (MS)



Invasive, but very sensitive (10^{-15} - 10^{-21} mol!!)



EI (electron impact) – hard ionisation



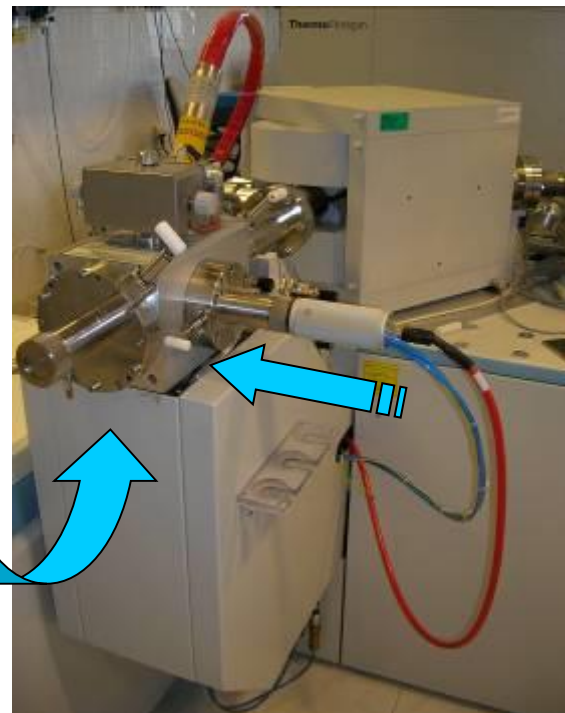
EI



Sample holder
→ 10-20 μg



Heated by program,
sample holding stick
200-300°C



Pros

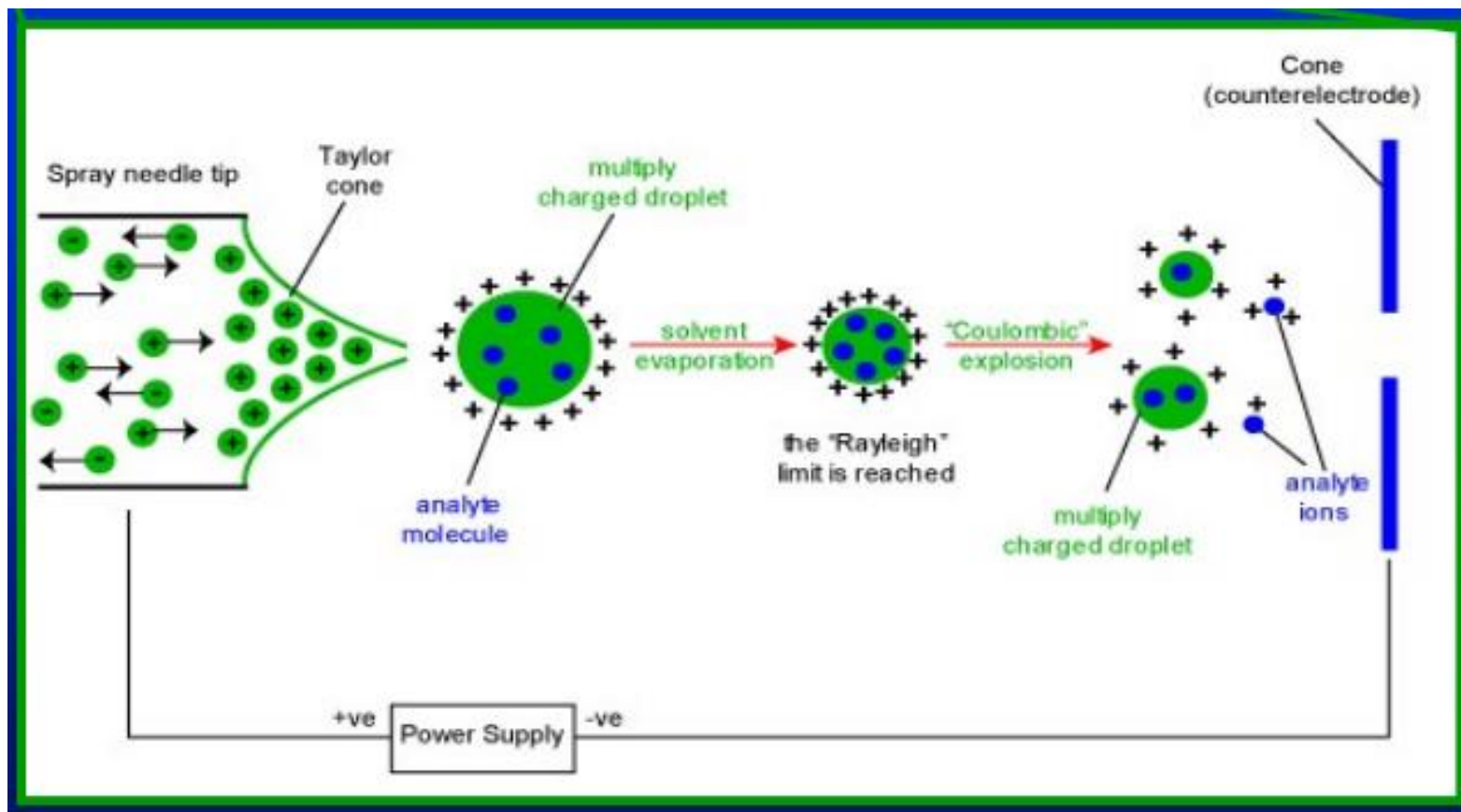
1. Most of small molecules
2. Lots of fragments
3. Programmed heating, some separation

Cons

1. M^+ is small, or not observable
2. Not suitable for thermally labile compounds

ESI (electrospray ionisation)– mild ionisation

Sample
in
solution

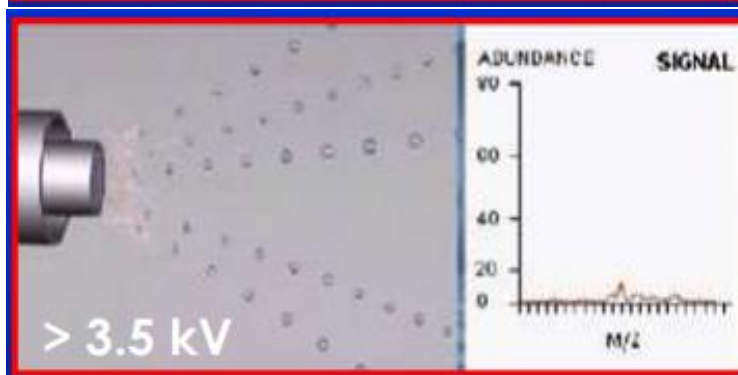
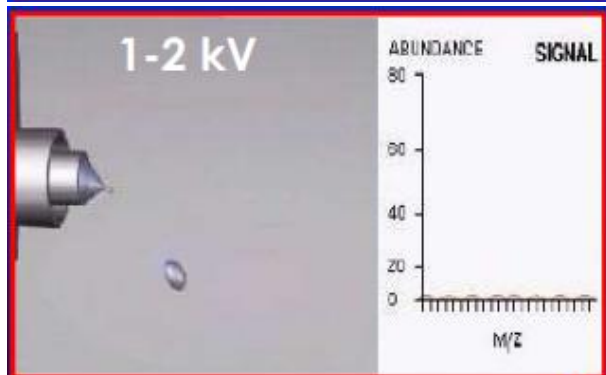
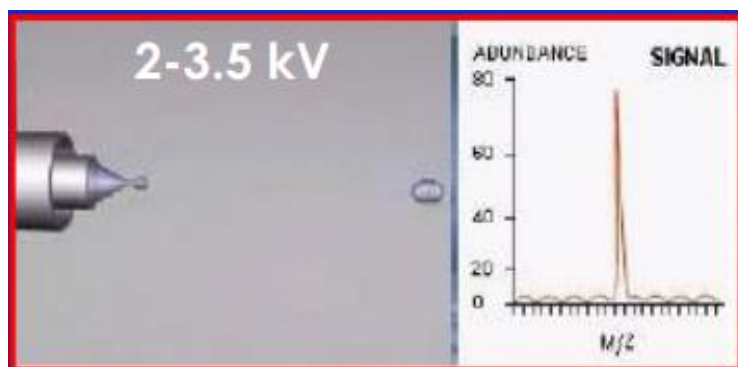
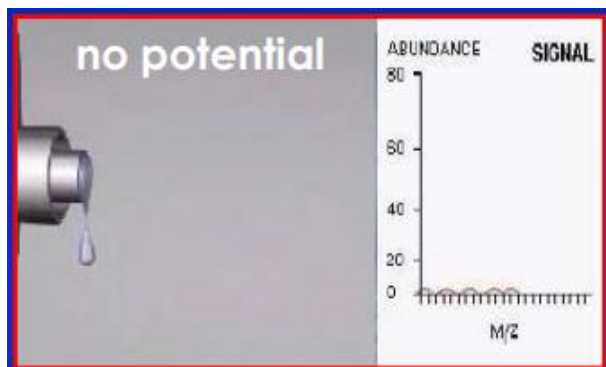
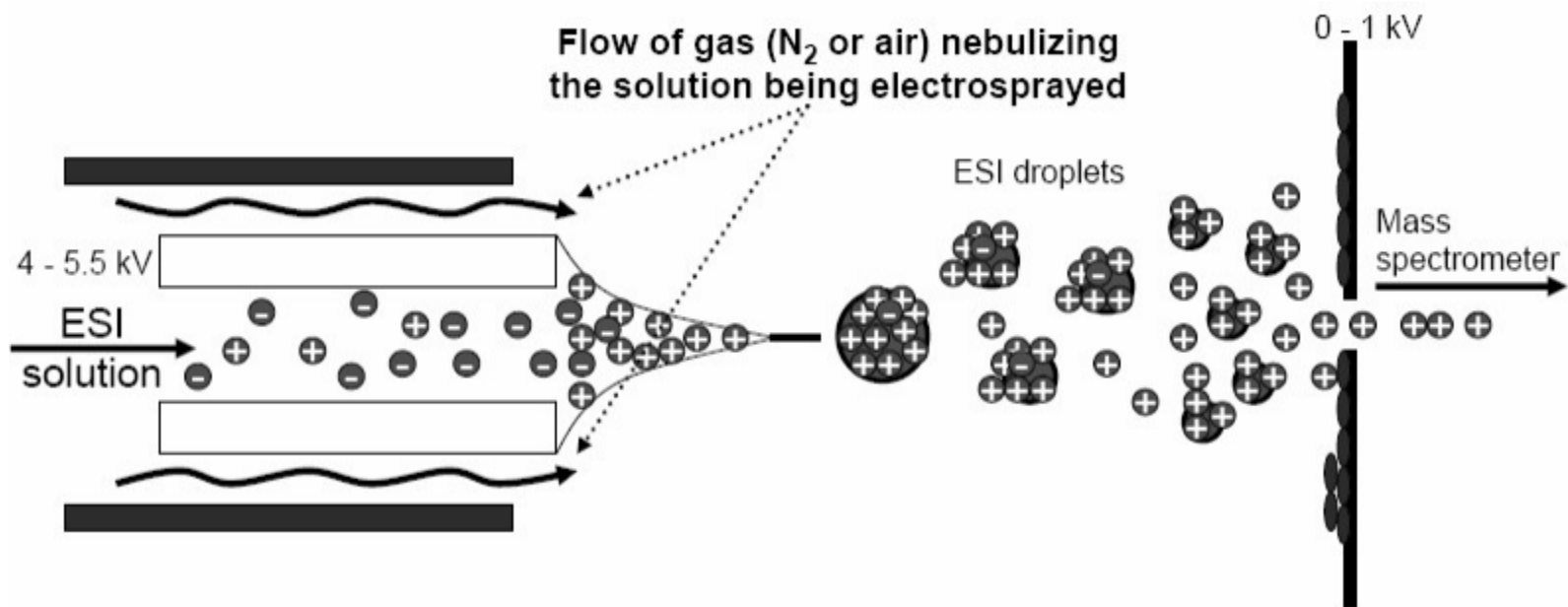


MeOH, AcCN, H₂O

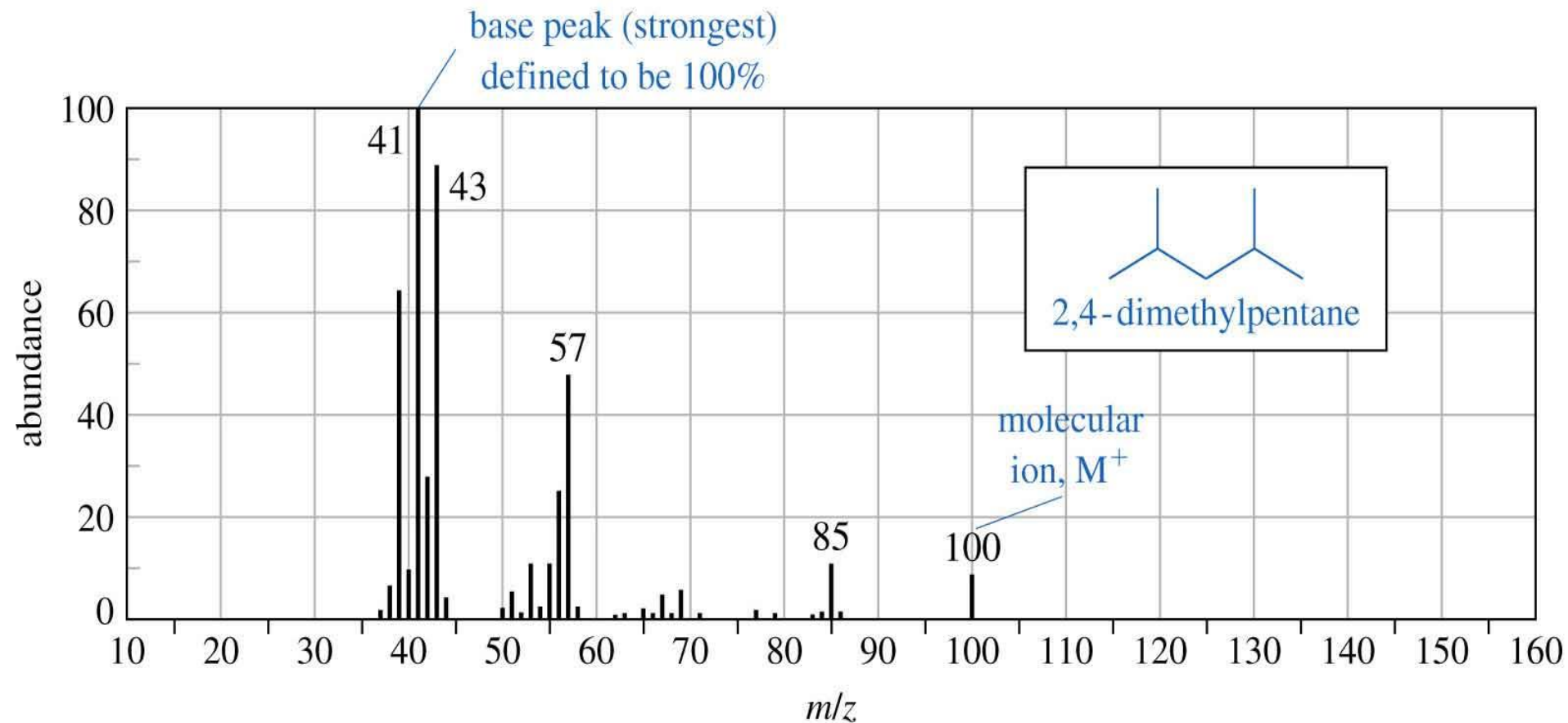
MH⁺, MHsolv⁺, M+Na⁺

Negative mode is also possible!

Sample inlet directly (in solution) or coupled with LC

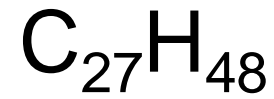
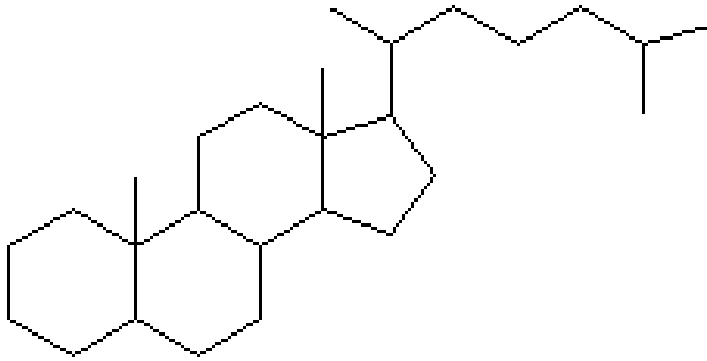


MS Spectrum



Under given circumstances the spectrum is relevant to the molecule!

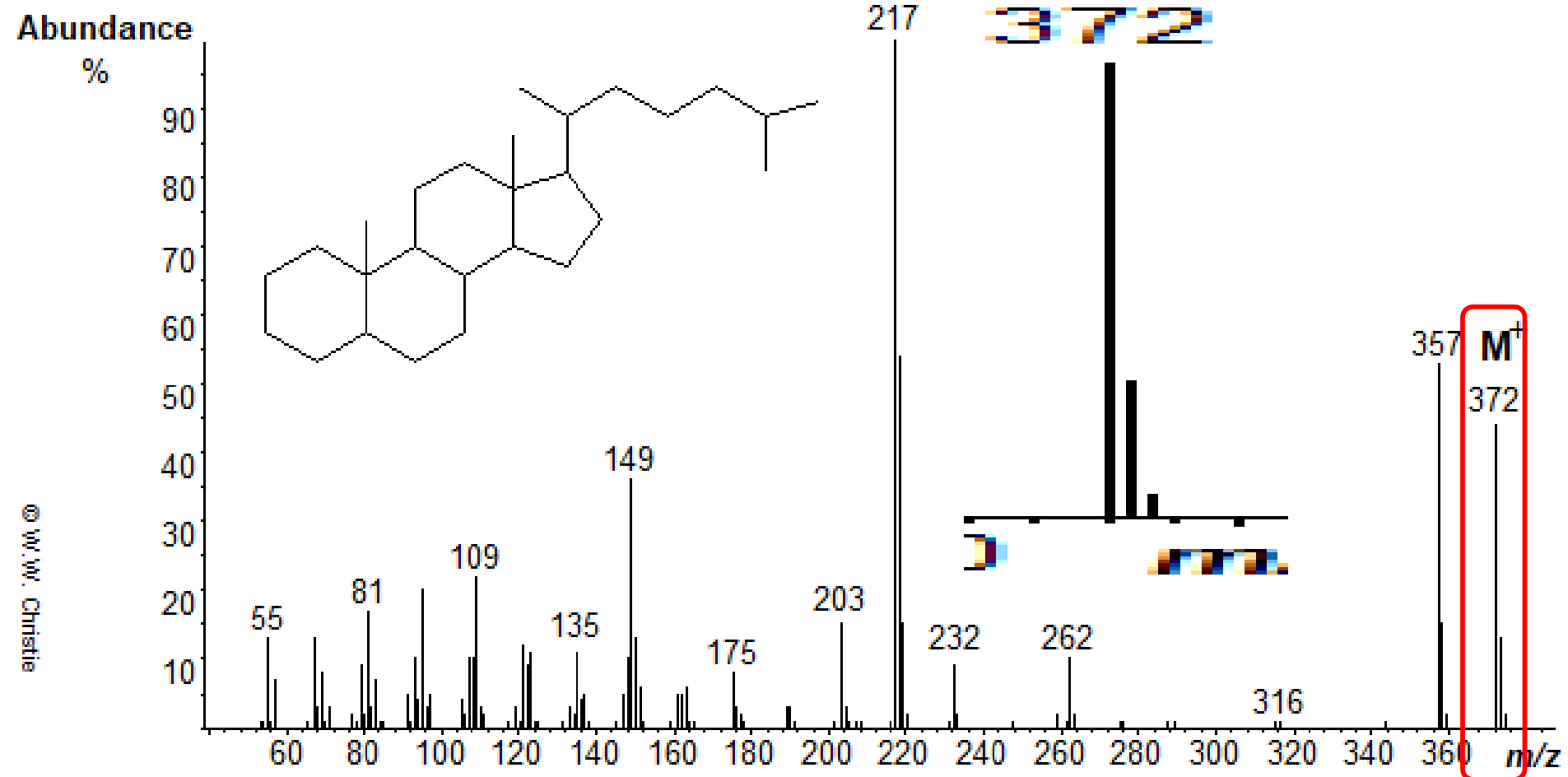
What do we expect?



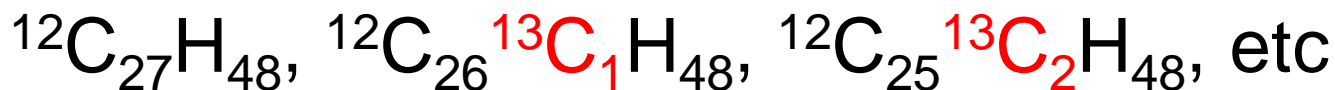
Periodic Table of the Elements

1 H 1.01																	18 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 51.99	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.73	32 Ge 72.61	33 As 74.92	34 Se 78.09	35 Br 79.90	36 Kr 84.10

M=372

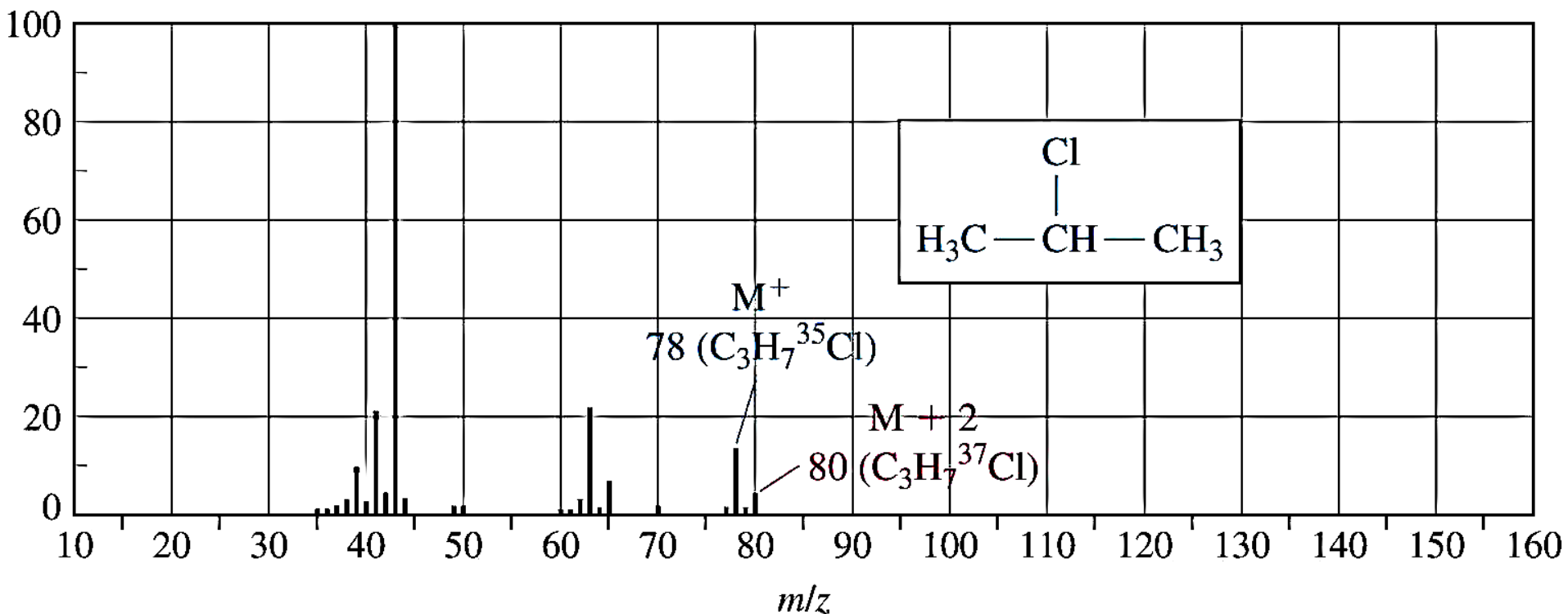
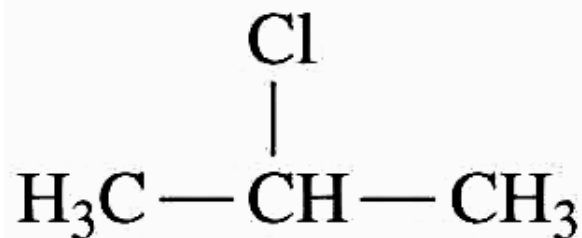


Every molecule is detected separately!!!

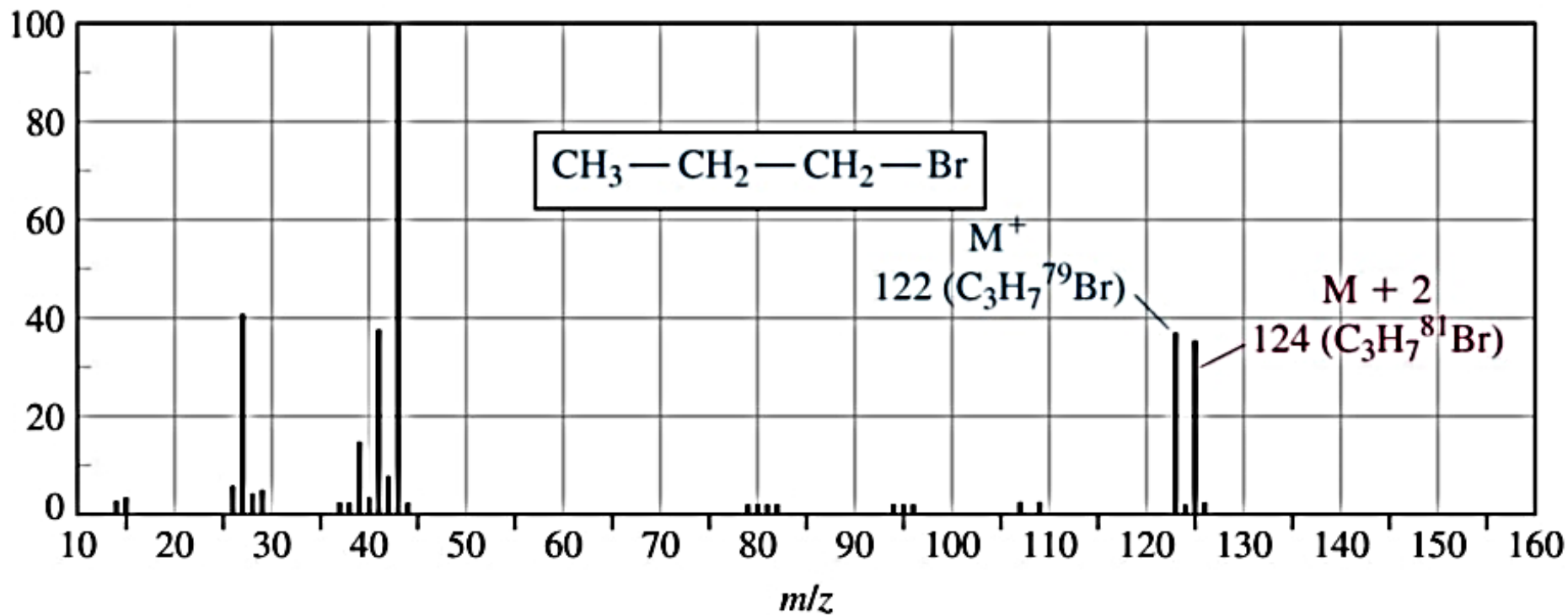


^{13}C has 1,1% abundance: $I(M+1)/I(M) \sim N(\text{C})$

MS spectrum of chlorine containing molecule



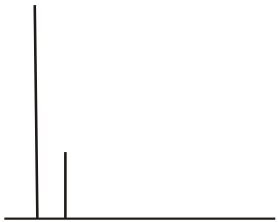
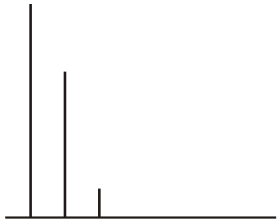
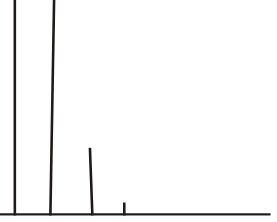
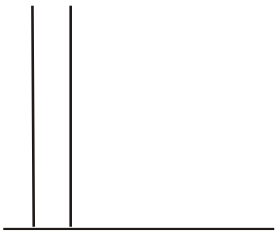
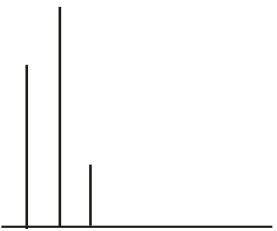
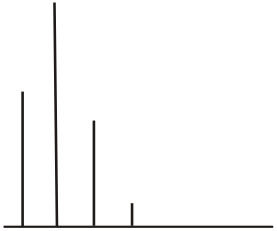
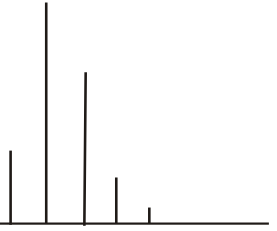
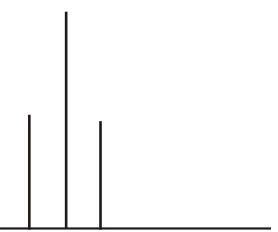
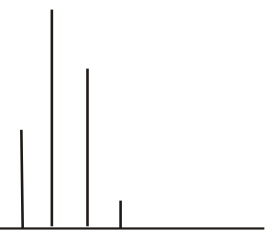
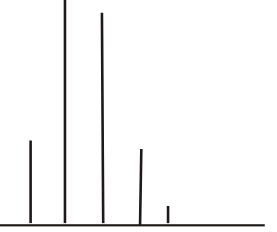
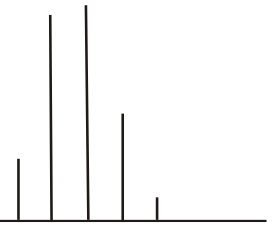
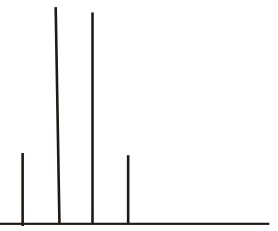
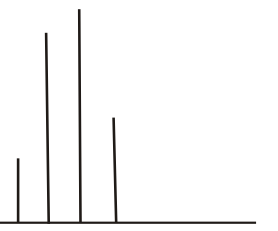
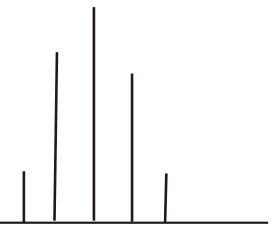
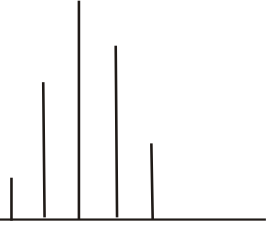
MS spectrum of bromine containing molecule



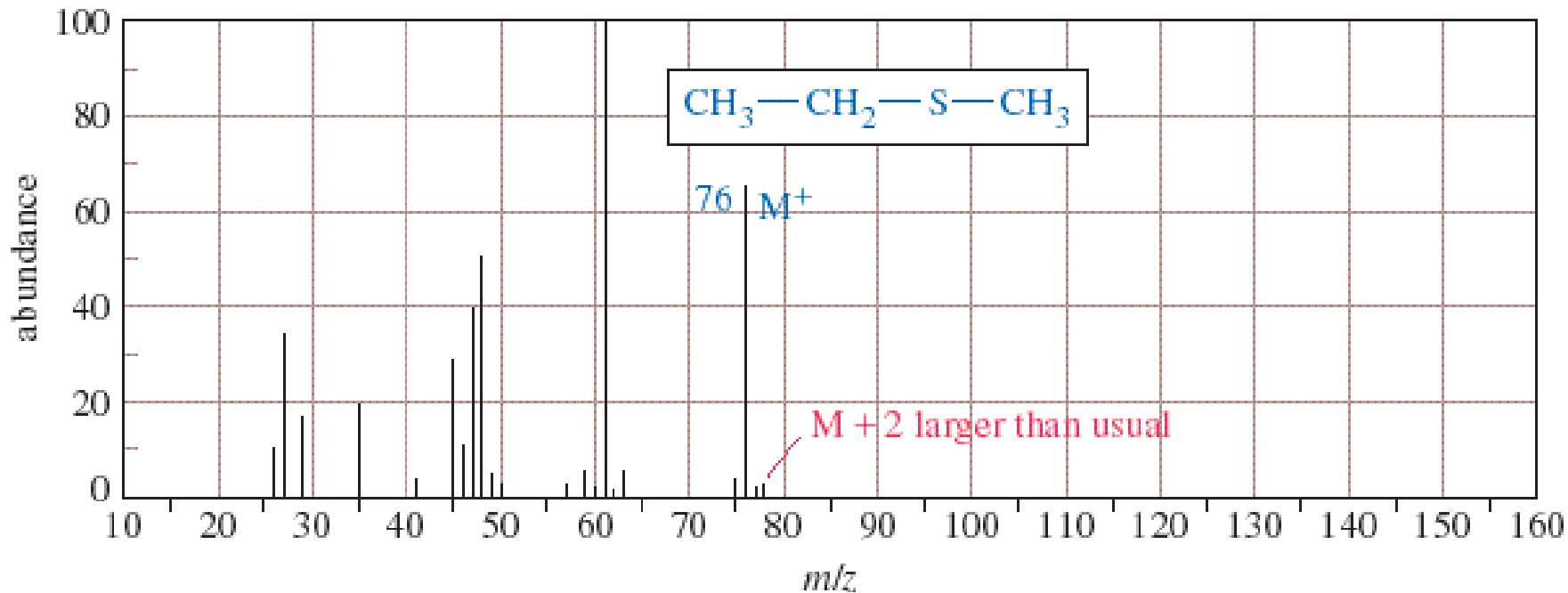
Izotop ratios

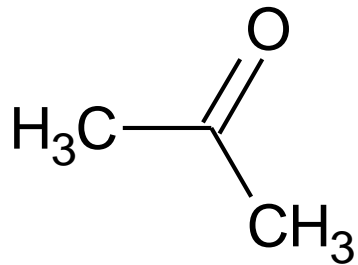
Most abundant	Less abundant	Ratio		
^{12}C	^{13}C	100	1.1	M+1
^{16}O	^{18}O	100	0.2	M+2
^{35}Cl	^{37}Cl	100	32.5	M+2 <i>ca</i> 3:1
^{79}Br	^{81}Br	100	98	M+2 <i>ca</i> 1:1
^{32}S	^{34}S	100	5	M+2

Isotope ratios if more halogens are present

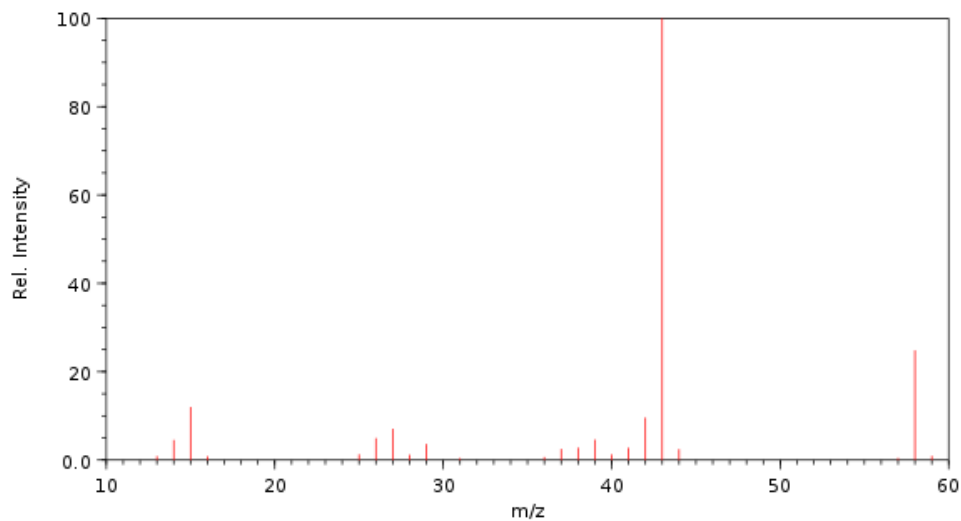
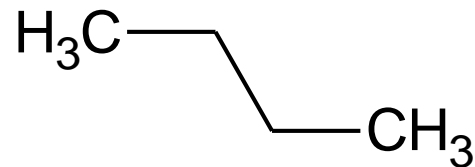
	—	Cl	Cl ₂	Cl ₃
—				
Br				
Br ₂				
Br ₃				

MS spectrum of sulphur containing molecule

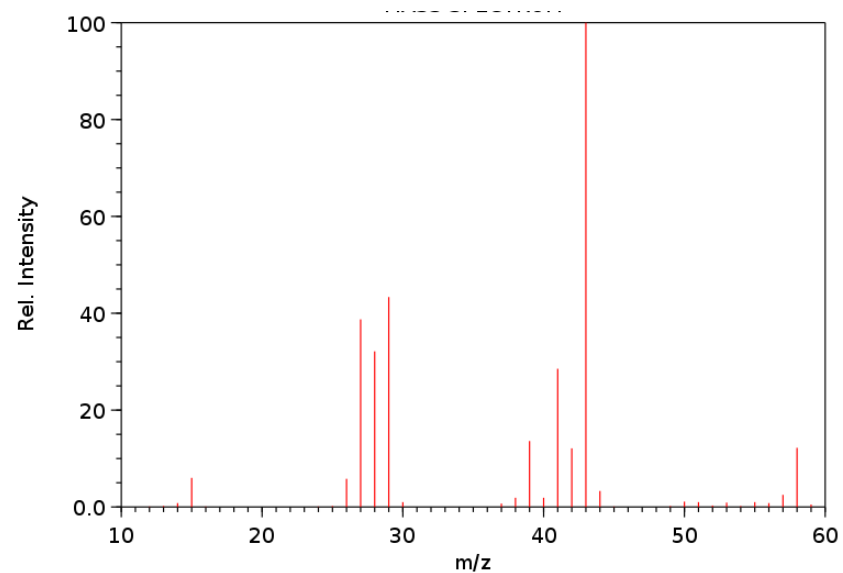




M=58!



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

Nominal mass

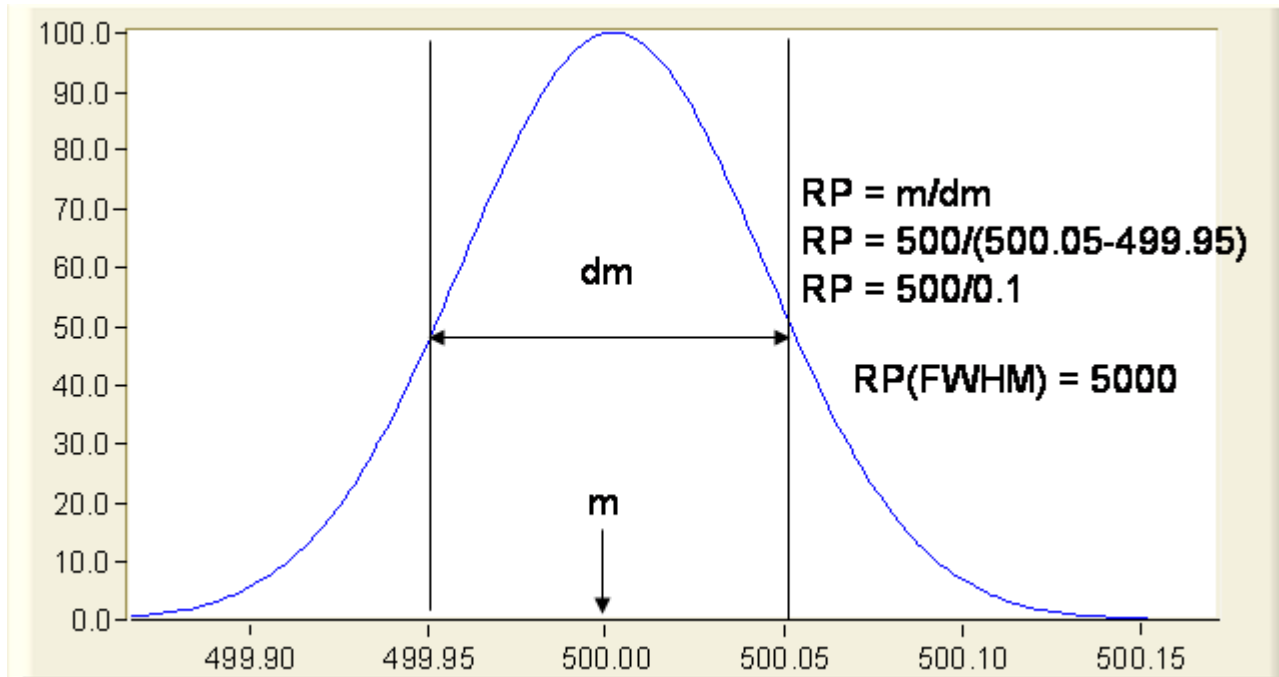
$m/z = 120$		M	M (%)	M+1 (%)	M+2 (%)
	$C_2H_4N_2O_4$	120,017107	100	3,15	0,84
	$C_2H_6N_3O_3$	120,040916	100	3,52	0,65
	$C_3H_{12}N_4O$	120,101111	100	5,00	0,31
	$C_4H_{12}N_2O_2$	120,089878	100	5,36	0,52
	$C_6H_6N_3$	120,056172	100	7,72	0,26
	C_9H_{12}	120,093900	100	9,92	0,44

$m(N)+2m(H) \neq m(O)$

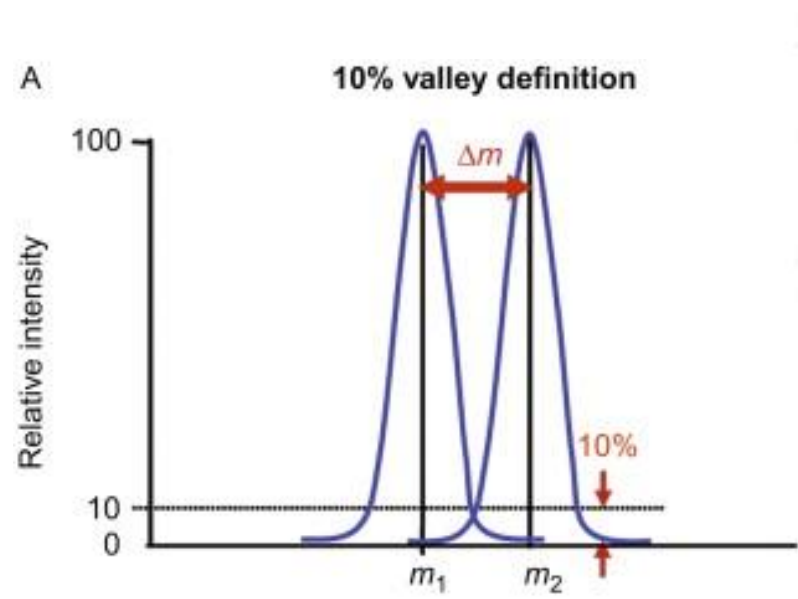
Mass defect

HRMS: High Resolution Mass Spectrum

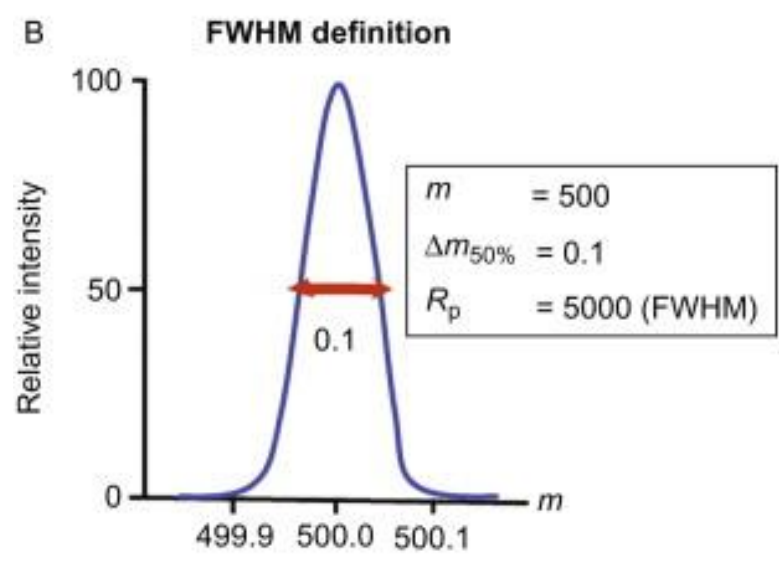
Resolution in MS



FWHM: Full width at half maximum



CO = 27.9949	}	$\Delta M = 0.0112$ $M/\Delta M = 2500$
N ₂ = 28.0061		
C ₂ H ₄ = 28.0313	}	$\Delta M = 0.0252$ $M/\Delta M = 1110$



Nominal
mass

Monoisotopic
mass

$m/z = 120$		M	M (%)	M+1 (%)	M+2 (%)
	$C_2H_4N_2O_4$	120,017107	100	3,15	0,84
	$C_2H_6N_3O_3$	120,040916	100	3,52	0,65
	$C_3H_{12}N_4O$	120,101111	100	5,00	0,31
	$C_4H_{12}N_2O_2$	120,089878	100	5,36	0,52
	$C_6H_6N_3$	120,056172	100	7,72	0,26
	C_9H_{12}	120,093900	100	9,92	0,44

How much R is needed? **R>30000**

Homework 3

Pipobroman is an anticancer drug. Calculate its M^+ , sketch its EI MS spectrum between m/z 350-360, give explanation.

Does it have characteristic IR absorption bands? If yes, which group, what wavenumber?

